'ate of California

#### 4 E M O R A N D U M

To : Jack Parnell, Director

Department of Food and

Agriculture

ames D. Boyd

Date : January 15, 1988

Subject: ARB Monitoring

of Azinphos-methyl

Executive Off-cer From : Air Resources Board

in response to your request of September 1, 1986, the ARB has conducted air monitoring for pesticidal uses of azinphos-methyl. This request was made by the Department of Food and Agriculture (DFA) pursuant to Division 7, Chapter 3, Article 1.5, Section 14021. The monitoring results and

additional background information are included in the attachments to this memorandum.

The azinphos-methyl monitoring was conducted in Kern County. A summary table of the monitoring results is presented in Attachment 1. Several actions were taken to select possible sampling sites. These actions included numerous meetings with DFA staff, meetings with representatives of the Agricultural Commissioner's Office of Kern County, and aerial and ground surveys of possible monitoring locations. A chronology of these events has been included as Attachment II.

Five locations in Kern County were selected as sampling sites. A background site was selected at Bakersfield. Sampling was conducted four days each week from June 22 to July 16, 1987. Sampling was conducted to coincide with azinphos-methyl applications to almond orchards for the control of navel orangeworms. The complete results of the monitoring and analysis are included in Attachments III and IV. Quality assurance reports are contained in Attachment V.

If you have questions regarding this submittal, please contact me at 5-4383 or have your staff contact Robert Barham, Chief, Toxic Air Contaminant Identification Branch, at 2-7072.

Attachments

cc: Dr. Michael Lipsett, DHS Citron Toy, Kern Co. APCD Bob Edwards, Kern Co. Agricultural Commissioner Robert Barham

# Attachments to the Transmittal Memorandum on Azinphos-methyl Monitoring Data January 1988

Attachment 1:

Summary Table

Attachment 11:

Chronology of Events

Attachment !!!:

UCD Report on Ambient

Concentrations of Azinphos-

methyl

Attachment IV:

Analysis Method

Attachment V:

Quality Assurance Reports

Attachment | Summary Table

Summary Table
Summary of Air Concentrations of Azinphos-methyl in Parts Per Trillion Volume (24-hour samples collected in June and July 1987)

	Maximum Positive <sup>a</sup>	Second Highest Positive <sup>2</sup>	Average All Samples above MDL	Total # of Samples analyzed	# Above MDL <sup>b</sup>
Pond	8.4	4.6	3.4	22	11
McFarland					
Learning Center	4.1	3.0	2.9	30	10
Browning Road School	5.9	2.7	2.7	28	25
Wasco	2.6	1.6	2.0	30	3
Shafter	2.2°	<mdl< td=""><td>2.2 _ ·</td><td>30</td><td>1</td></mdl<>	2.2 _ ·	30	1
Bakersfield	2.2	<mdl< td=""><td>2.2</td><td>30</td><td>2</td></mdl<>	2.2	30	2

<sup>\*</sup>Average of two replicates

bMDL = Minimum detection limit (1.7 ppt)

Only one replicate

Attachment II Chronology of Events

# Azinphos-methyl Monitoring Chronology of Major Events

September 1, 1986

April 27, 1987

May 8, 1987

June 3, 1987

June 22 -July 16, 1987

December 1987

DFA requests ARB to monitor azinphos-methyl.

UCD submits work plan for azinphos-methyl sampling.

ARB submits work plan for azinphos-methyl analysis.

ARB staff meets with representatives of UCD and Kern County Agricultural Commissioner's Office regarding azinphos-methyluse and sampling locations.

Sampling is conducted at Kern County sites.

UCD submits draft report to ARB.

# Attachment III

UCD Report on Amblent Concentrations of Azinphos-methyl

# Final Report to the Air Resources Board

Pilot Analysis of Azinphos-Methyl in Air

Contract # A5-169-43

Date: January 4, 1988

James N. Seiber

M. M. McChesney

J. E. Woodrow

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Department of Environmental Toxicology University of California, Davis

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# Summary

Air sampling for Azinphos-methyl was conducted during June and July, 1987, at five ambient locations in Kern County (Figure 1). A background site was established in the city of Bakersfield. Samples were also collected at an almond orchard application site located northeast of the town of McFarland prior to, during and 16 hours after the application of azinphos-methyl to an almond orchard.

The samples were collected in XAD-4 samplers and analyzed by a gas chromatographic method. Table I has the summary of results. The highest concentrations of azinophos methyl (8.4 parts per trillion or 109 ng/m³) were found near the town of Pond; the average of all positive samples at this site was 3.4 ppt (44 ng/m³). At the application site only one sample gave a positive response at the minimum detection limit (MDL) of 1.7 ppt (22 ng/m³).

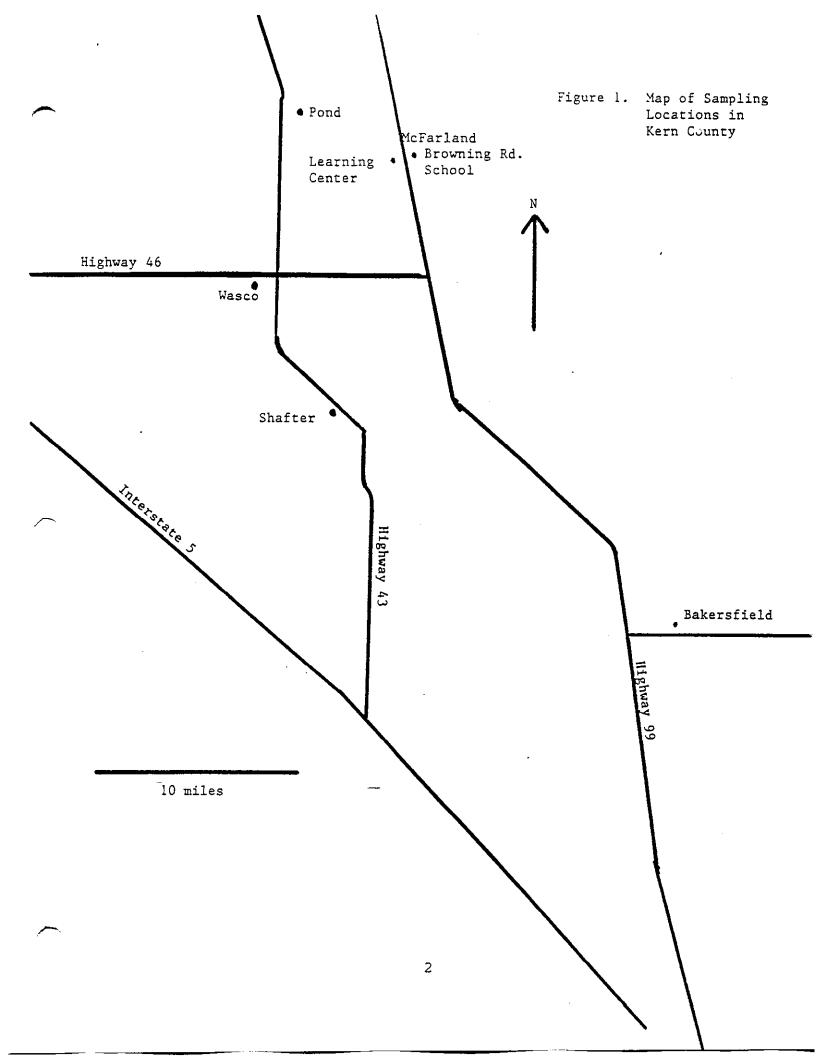


Table 1. Summary of Air Concentrations of Azinphos-methyl in Parts Per Trillion Volume

	Maximum Positive <sup>a</sup>	Second Highest Positive <sup>a</sup>	Average All Samples above MDL	Total # of Samples analyzed	# Above MDL <sup>b</sup>
Pond	8.4	4.6	3.4	22	11
McFarland					
Learning Center	4.1	3.0	2.9	30	10
Browning Road School	5.9	2.7	2.7	2,8	25
Wasco	2.6	1.6	2.0	30	3
Shafter	2.2°	<mdl< td=""><td>2.2</td><td>30</td><td>1</td></mdl<>	2.2	30	1
Bakersfield	2.2	<mdl< td=""><td>2.2</td><td>30</td><td>2</td></mdl<>	2.2	30	2

<sup>&</sup>lt;sup>a</sup>Average of two replicates

bMDL = Minimum detection limit (1.7 ppt)

<sup>&</sup>lt;sup>c</sup>Only one replicate

### Introduction

Azinphos-methyl is extensively used in agriculture (383,565 lbs for 1985 in California [1]). The time-weighted average (8 hr/day, 40 hr/wk) threshold limit value for azinphos-methyl in air is 15 ppb [2].

In this study low volume (2.0 L/min) ambient air samples were collected in Kern County for azinphos-methyl analysis at five sites plus a background site. Also, an application site was monitored prior to, during, and 16 hours following completion of the application. Ambient air samples were taken over a four week period from June 22 to July 16, 1987.

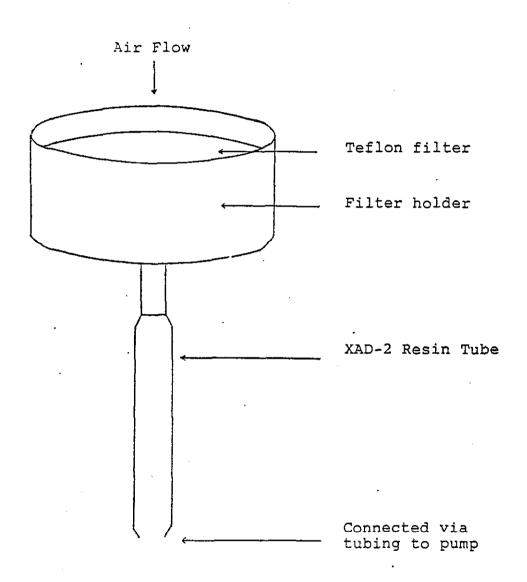
### Experimental

## Site Selection and Sampling

# Ambient Sites

Five sites were selected in Kern County, at the following locations: Pond Unified School, Pond; Browning Road School, McFarland; McFarland Learning Center, McFarland; Kern County Engine company No. 31, Wasco; Richland School District Office, Shafter. A background site was established at the Air Resources Board monitoring site in Bakersfield. All samplers, with the exception of that at the Wasco site, were located on roof tops. The Wasco site sampler was positioned on top of a 25-foot hose tower. Each site met the ARB siting criteria and passed the ARB site audit performed on July 7, 1987.

Figure 2. Filter with XAD-2 Resin Tube



#### Sampling

Azinphos-methyl samplers consisted of a XAD-2 resin tube connected to a Teflon filter via latex tubing, as shown in Figure 2. The top two thirds of the tube was the primary trap while the bottom third of the tube was the back-up. The entire "sample" was wrapped in aluminum foil to prevent sunlight from striking the tubes and thus heating them or causing photodegradation. After sampling was completed the tubes were kept on dry ice until transported to U.C. Davis, where they were kept at -20°C. Samples were kept on dry ice while being delivered to the ARB for analysis.

Four replicates were collected at the Browning Road School site; two replicate samples were taken at the other sites. Replicate samples were taken two meters apart and 1.67 meters above the roof top. One sampler was marked "A" and designated as the primary sample (as per ARB protocol) while the "B" sampler was the replicate. The samplers were connected to high volume sampling pumps via 3/8 inch Tygon tubing and a "T" open to the air. The "T" was needed to step down to the desired flow rate. The flow rates were regulated by pinch clamps on the open end of the "T". Flow rates were measured by attaching a flow meter to the top (open) end of each sampler at the beginning and the end of the sampling period. Trapping studies, completed prior to any sampling indicated that the maximum sampling period without breakthrough was 24 hrs with a flow rate of 2.0 LPM. A listing of sources of equipment and supplies used for field sampling is in Table 2. Flow rates at the ambient sites ranged from a minimum of 1.2 to a maximum of 2.3 and an average of 1.7 LPM. Total air volumes for sampling periods ranged from a minimum of 1.5 to a maximum of 3.4 and an average of 2.3 cubic meters. These are the flow ranges for different air samplers; for individual samplers, the air flows remained constant during a 24-hr sampling period and were accurately measured for eventual calculation of air concentrations.

Samples were coded using the month and day. A letter followed which represented the site: A, Bakersfield; B, Shafter; C, Wasco; D, the Learning Center in McFarland; E, Browning Road School, McFarland; F, Pond Unified School, Pond. The next number indicated whether the sample was primary (1) or a replicate (2). The last letter signified if the sample was either resin (R) or a filter (F).

### Application Site

A single sampling site was set out during and following application to an almond orchard located at Browning and Peterson Roads northeast of McFarland (Figure 3). The sampling site was located approximately 0.25 miles south and 0.1 miles east of the applied field. The wind patterns changed during the day with calm conditions during the application, a northwest wind from the early to midmorning, then changing direction and becoming very strong out of the west during the late afternoon. Application was started at 6:30 a.m. on July 16 and completed within one hour. Duplicate samples consisting of XAD-4 resin only and flow rates of 50 L/min were taken during the intervals 6:30 to 7:30 (during application) and 7:30 to 12:00 following application, at a sampling height of 1.7 m. Table 3 contains the sampling intervals for the application site.

#### Laboratory Analysis

All samples were analyzed by ARB. The analytical procedure for azinphos-methyl is contained in Attachment IV of the final report to the Department of Food and Agriculture.

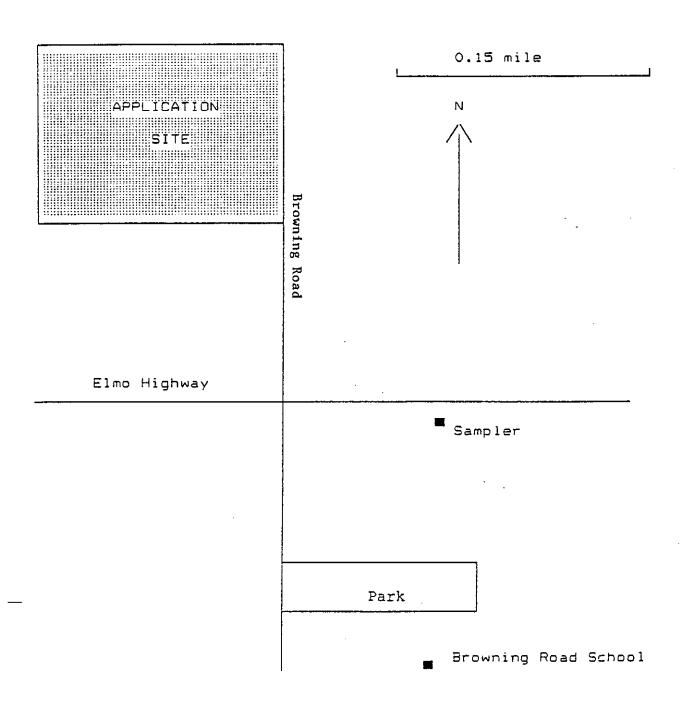
Table 2. List of Equipment for Field Work

- 1. Wind Profile Register system, Model 104-LED-LM-DC CWT-1791, Thornwaite and Associates, Elmer, NJ
- 2. Microdatalogger, Model CR-21X, Campbell Scientific, Logan, UT
- 3. Temperature probe, Model 107, Campbell Scientific, Logan, UT
- 4. High volume air samplers, Model U-1/AT, BGI, Inc., Waltham, MA
- 5. High volume air sampler, Bendix Co., Baltimore, MD
- 6. Resi-Grade Methanol, Acetone, Ethyl Acetate, Methylene Chloride, Baker Chemical Co.
- 7. Rotameter, Model VFA 21, Dwyer Instruments, Inc., Michigan City, IN
- 8. XAD-2 prepacked sampling tubes, SKC Inc., Eightyfour, PA
- 9. XAD-4 resin.

Table 3. Sampling at Application Site

Sample	Time On	Time Off	
During	6:25	7:25	
Post app. 1 hr	7:30	8:30	
Post app. 2 hr	8:35	10:35	
Post app. 4 hr	10:45	14:55	
Post app. 4 hr	15:05	19:00.	
Post app.	19:05	22:00	•

Figure 3. Application Site



#### Results

### Field Samples

Table 4 summarizes the field samples collected. Table 5 contains the ambient site results. Table 6 contains the comparison of replicates for ambient site samples, while Table 7 has the average concentration in ppt and ng/m³. Because of the variations in flow rates, the minimum detectable limit (MDL) varied from a minimum of 15 ng/m³ (1.1 ppt) to a maximum of 34 ng/m³ (2.6 ppt) with an average of 22 ng/m³ (1.7 ppt). All azinphos-methyl was trapped on the teflon filters. At the Wasco site one sampler was run with XAD only. Only one XAD tube sample at this site gave a positive value as did the collocated sampler with filter and resin tube.

The concentrations of Azinphos-methyl were highest at the Pond School site (8.4 ppt). The Pond Site has the "worst case situation" because of almond orchards directly to the east, south, and west located less than 100 meters from the sampler, while the distance from orchards to sampler was at least 0.25 miles at the other sites. However, the predominant daytime wind was from the north-northwest. Wind direction did change during the late evening hours and came from a southern direction.

## Application Site

Only one sample gave a positive result at the detection limit. All other samples were less than the MLD.

Table 4. Number of 24-hour Sampling Periods for Azinphos-methyl

			Stationary	y Sites		
Date	Bakersfield	Shafter	Wasco	Mc	Farland	Pond
Date	Dakersi lelu	Sharter	w asco	Learning Center	Browning Rd. School	Unified School
6/22	· x	X	x	X	X	-
6/23	X	X	X	x	x	X
6/24	x	X	X	x	x	X
6/25	X	X	X	X	x	•
6/29	X	x	X	X	, <b>x</b>	X
6/30	X	X	Х	-	X	-
7/1	X	X	X	X	-	-
7/6	x	X	X	X	x	X
7/7	x	X	X	X	x	x
7/8	X	$\mathbf{x}$	x	x	x	X
7/9	x	x	X	X	x	x
7/13	X	x	X	x	x	x
7/14	x	x	X	X	X	x
7/15	x	x	X	x	x	X
7/16	X	X	X	· X	$\mathbf{x}^{-}$	X

TABLE 5
AZINPHOS-METHYL AMBIENT SITES RESULTS

SAMPLE ID	DATE START	TIME START	DATE STOP	TIME STOP	PERIOD (HOURS)	(1pm)	((Cii m)	
62241R 6224A1F 6222B1R 6222B1R 6222C22C2R 6222C2C2C2C 6222C2C2C 6222C2C2C 6222C2C 6222C2C 6222C2C 6222C2C 6222C2C 622CC	6/22/87 6/22/87 6/22/87 6/22/87 6/22/87 6/22/87 6/22/87 6/22/87 6/22/87 6/22/87 6/22/87 6/22/87 6/22/87	945 945 945 1535 1415 1315 1315 1320 1220 1220	6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87	1205 1205 1205 1205 1114 1114 1037 1037 825 825 825 730 730 730	26.3 26.3 26.3 19.7 19.7 20.4 19.2 19.2 19.2 19.2 19.2	1.52 1.57 1.52 1.57 1.57 1.57 1.76 1.76 1.42 1.42 1.57 1.76	2.54588225454801.20.1	
622E3F 622E3F 622E4R 622E4R 622E1F 622EF 622EF 622EF 622EF 622EF 622EB 62EB 6	6/22/87 6/22/87 6/22/87 6/22/87 6/22/87 6/22/87 6/22/87 6/22/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87	1220 1220 1220	6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/24/87 6/24/87 6/24/87 6/24/87 6/24/87 6/24/87	730 730 730 730 730 717 917 917 1405 1405 1317 1248 1123 1123	19.22.22.22.35.00.11777772.22.22.22.35.5.00.11777777	1.66 1.57 1.76 1.86 1.66 2.10 2.05 2.10 1.57 1.57 1.57 1.77 1.47 1.47	1.201.978784544881313	O.07
623E1F 623E3F 623E1R 623E1R 623E1R 623E3F 623E5F 62	6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/23/87 6/24/87	905 905 905 905 905 905 905 905	6/24/87 6/24/87 6/24/87 6/24/87 6/24/87 6/24/87 6/24/87 6/24/87 6/24/87 6/24/87 6/24/87 6/25/87 6/25/87	1047 1047 1047 1047 1047 1047 1047 1205 1205 1205 1258 1258 1215	26.7 26.7 26.7 26.7 26.7 27.5 26.7 26.7 27.5 28.2 28.2 28.2 28.2 28.2 28.2 28.2 28	1.37 1.66 1.81 1.71 1.37 1.66 1.81 1.71 1.76 2.15 1.76 2.15 1.57	12279727978484100 2222222223232323	•

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Table 5 (cont.)
AZINPHOS-METHYL AMBIENT SITES RESULTS

SAMPLE ID	DATE START	TIME START	DATE STOP	TIME STOP	PERIOD (HOURS)	FLOW RATE (lpm)	AIR VOLUME ((Cu m)	_
624B2R	6/24/87	1321	6/25/87	1215	22.9	1.57	2.2	
624C1R	6/24/87	1255	6/25/87	1138	22.7	1.66	2.3	
624C2R	6/24/87	1255	6/25/87	1138	22.7	1.86	2.5	
624D1F	6/24/87	1136	6/25/87	1005	22.5	1.37	1.9	
624D2F 624D1R	6/24/87	1136	6/25/87	1005 1005	22.5	1.42	1.9	
624D2R	6/24/87 6/24/87	1136 1136	6/25/87 6/25/87	1005	22.5 22.5	1.37 1.42	1.9	
624E1F	6/24/87	1109	6/25/87	923	55.5	1.76	1.9 2.4	0.18
624E2F	6/24/87	1109	6/25/87	723	22.2	1.71	2.3	0.18
624E3F	6/24/87	1107	6/25/87	923	22.2	1.57	2.3	0.14
624E4F	6/24/87	1107	6/25/87	923		1.66	2.2	0.18
624E1R	6/24/87		6/25/87	923	22.2	1.76	2.4	0.10
624E2R	6/24/87		6/25/87	923	22.2	1.71	2.3	
624E3R	6/24/87		6/25/87	923	22.2	1.57	2.1	
624E4R	6/24/87		6/25/87	923	22.2	1.66	2.2	
624F1F	6/24/87		6/25/87	1042	22.4	2.05	2.8	
624F2F	6/24/87	1218	6/25/87	1042	22.4	2.05	2.8	
624F1R	6/24/87	1218	6/25/87	1042	22.4	2.05	2.8	
624F2R	6/24/87		6/25/87	1042	22.4	2.05	2.8	
625A1F	6/25/87		6/26/87	1230	23.4	1.42	2.0	
625A2F	6/25/87		6/26/87	1230	23.4	1.37	1.9	
625A1R	6/25/87		6/26/87	1230	23.4	1.42	2.0	
625A2R	6/25/87		6/26/87	1230	23.4	1.42	2.0	
625B1F	6/25/87		6/26/87	1151	23.6	1.37	1.9	
625B2F	6/25/87	1218	6/26/87	1151	23.6	1.37	1.9	
625B1R 625B2R	6/25/87 6/25/87	1218 1218	6/26/87 6/26/87	1151 1151	23.6 23.6	1.37 1.37	1.9 1.9	
62562F	6/25/87	1145	6/26/87	1120	23.6 23.6	1.37	1.7	0.07
625C1R	6/25/87	1145	6/26/87	1120	23.6	1.71	2.4	0.05
625C2R	6/25/87	1145	6/26/87	1120	23.6	1.37	1.9	0.03
625D1F	6/25/87	1005	6/26/87	1120	13.9	0.11	0.1	
625D2F	6/25/87	1005	6/26/87		13.9	0.11	0.1	
625D1R	6/25/87	1005	6/26/87		13.9	0.11	0.1	
625D2R	6/25/87	1005	6/26/87	,	_ 13.9	0.11	0.1	
625E1F	6/25/87	942	6/26/37	932	23.8	1.71	2.4	0.09
625E2F	6/25/87	942	6/26/87	932	23.8	1.57	2.2	0.08
625E3F	6/25/87	942	6/26/97	732	23.8	1.57	2.2	0.07
625E4F	6/25/87	942	6/26/87	932	23.8	1.66	2.4	0.08
625E1R	6/25/87	942	5/25/87	732	23.8	1.71	2.4	
625E2R	6/25/87	942	6/26/87	932	23.8	1.57	2.2	
625E3R 625E4R	6/25/87	942	6/25/87	932	23.8	1.57	2.2	
625F1F	6/25/87 6/25/97	942 1055	6/25/87 5/25/37	932 1039	23.9 23.7	1.66 2.05	2.4 2.9	0.07
625F2F	6/25/87	1055	6/26/37	1037	23.7	2.10	3.0	0.07
625F1R	6/25/87	1055	5/25/37	1037	23.7	2.05	2.9	C. C.
625F2R	6/25/87	1055	5/25/37	1037	23.7	2.10	3.0	
627A1F	5/29/87	1500	6/30/87	1508	24.1	1.47	2.1	0.07
629A2F	5/29/87	1500	6/30/87	1508	24.1	1.47	2.1	0.05
629A1R	5/29/87	:500	6/30/E7	:508	<b>34.1</b>	1.47	⊇.1	
				14				

Table 5 (cont.)
AZINPHOS-METHYL AMBIENT SITES RESULTS

SAMPLE I D	DATE START	TIME START	DATE STOP	TIME STOP	PERIOD (HOURS)	FLOW RATE (lpm)	AIR VOLUME ((Cu m)	AZINPHOS METHYL (rg)
			=======			=======		=======
629A2R	6/29/87	1500	6/30/87	1508	24.1	1.47	2.1	
629B1F	6/29/87	1415	6/30/57	1340	23.4	1.62	2.3	
629B2F	6/29/87	1415	6/30/87	1340	23.4	1.57	2.2	
629B1R	6/29/87	1415	6/30/87	1340	23.4	1.62	2.3	
629B2R	6/29/87	1415	6/30/87	1340	23.4	1.57	2.2	
629C2F	6/29/87	1315	6/30/87	1238	23.4	1.66	2.3	0.05
629C1R	6/29/87	1315	6/30/87	1238	23.4	1.81	2.5	
629C2R	6/29/87	1315	5/30/87	1238	23.4	1.66	2.3	
629D1F	6/29/87	1135	6/30/87	1107	23.5	1.37	1.9	0.08
629D2F	6/29/87	1135	<i>5</i> /30/87	1107	23.5	1.37	1.9	0.07
629D1R	6/29/87	1135	<i>5</i> /30/87	1107	23.5	1.37	1.9	
629D2R	6/29/87	1135	6/30/87	1107	23.5	1.37	1.9	
629E1F	6/29/87	1038	5/30/87	1019	23.7	1.62	2.3	0.07
629E2F	6/29/87	1038	5/30/87	1019	23.7	1.62	2.3	0.08
629E3F	6/29/87	1038	6/30/87	1019	23.7	1.62	2.3	0.07
629E4F	6/29/87	1038	6/30/87	1019	23.7	1.71	2.4	0.07
629E1R	6/29/87	1038	6/30/87	1019	23.7	1.62	2.3	
629E2R	6/29/87	1038	6/30/87	1019	23.7	1.62	2.3	
629E3R	6/29/87	1038	6/30/87	1019	23.7	1.62	2.3	
629E4R	6/29/87	1038	6/30/87	1019	23.7	1.71	2.4	
629F1F	6/29/8 <b>7</b>	1230	6/30/87	1230	24.0	2.20	3.2	0.05
629F2F	6/29/87	1230	6/30/87	1230	24.0	2.15	3.1	
625F1R	6/29/87	1230	6/30/87	1230	24.0	2.20	3.2	
629F2R	6/29/87	1230	5/30/B7	1230	24.0	2.15	3.1	
530A1F	6/30/87	1515	7/1/87	1202	20.8	1.47	1.8	
630A2F	6/30/87	1515	7/1/87	1202	20.8	1.57	2.0	
630A1R	6/30/87	1515	7/1/87	1202	20.8	1.47	1.8	
630A2R	6/30/87	1515	7/1/87	1202	20.8	1.57	2.0	
630B1F	6/30/87	1358	7/1/87	1107	21.2	1.57	2.0	
630B2F	6/30/87	1358	7/1/87	1107	21.2	1.57	2.0	
630B1R	6/30/87	1359	7/1/87	1107	21.2	1.57	2.0	
630B2R	6/30/87	1358	7/1/87	1107	21.2	1.57	2.0	
430C2F	6/30/87	1250	7/1/87	1030	21.7	1.56	2.2	
630C1R	6/30/87	1250	7/1/87	1030	21.7	1.86	2.4	
630C2R	6/30/87	1250	7/1/87	1030	21.7	1.66	2.2	
630D1F 630D2F	6/30/87 6/30/87	1125	7/1/87		12.6	0.74	0.6	
	6/30/87	1125	7/1/37 7/1/87		12.6	0.84	0.6	
630D1R 630D2R	6/30/87	1125 1125	7/1/8/7/1/87		12.6 12.6	0.74 0.84	0.6	
5305ER 530E1F	6/30/87	1039	7/1/87	752	21.2	1.62	0.6 2.1	
530E2F	6/30/87	1037	7/1/87	752	21.2	1.81	2.3	
630E3F	6/30/87	1037	7/1/37	752 752	21.2	1.55	2.1	0.06
530E4F	6/30/87	1037	7/1/37	752	21.2	1.71	2.2	3,50
530E1R	6/30/87	1037	7/1/87	752	21.2	1.62	2.1	
630E2R	6/30/87	1039	7/1/87	752	21.2	1.81	2.3	
530E3R	6/30/87	1039	7/1/87	752	21.2	1.66	2.1	
530E4R	5/30/87	1039	7/1/87	752	21.2	1.71	2.2	
71A1R	7/1/87	1211	7/2/97	845	20.6	1.57	1.9	
71A1R	7/1/3 <b>7</b>	:211	7/2/87	34 <b>5</b>	20.5	1.47	1.8	
				15				

Table 5 (cont.)
AZINPHOS-METHYL AMBIENT SITES RESULTS

SAMPLE ID	DATE START	TIME START	DATE STOP	TIME STOP	PERIOD (HOURS)	FLOW RATE (lpm)	AIR VOLUME ((Cu m)	_
== 77777777777777777777777777777777777	ST = 7/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1	STATE 11111111111111111111111111111111111	TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT	5T0P==0444448888000044444222277778888888888888	T7777000555550000555500002222111111119999900055550000222211111111999990005555555555	(1p==-666661177777772726476712727266766266505027272222 1.77771117777772726767161111111111111111	## 22222329292454949434378745454775477540405454222 ## 222223292924545454775477540405454222 (##	(µg)
7782R 7702F 7701R 7702R	7/7/87 7/7/87 7/7/87 7/7/87	1220 1258 1259 1258	7/8/87 7/8/87 7/8/87 7/8/87	1050 1007 1007 1007	22.5 21.2 21.2 21.2	1.62 1.62 1.71 1.62	2.2 2.1 2.1	

Table 5 (cont.)
AZINPHOS-METHYL AMBIENT SITES RESULTS

SAMPLE ID	DATE START	TIME START	DATE STOP		PERIOD (HOURS)	FLOW RATE (lpm)	AIR VOLUME ((Cu m)	AZINPHOS METHYL (+g)
77D1F 77D11R 77D12R 77D12R 77D12R 77D7777777777777777777777777777777777	7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/7/87 7/8/87	1350 1350 1350 1017 1017 1017 1017 1017 1017 1017 10	7/8/87 7/8/87 7/8/87 7/8/87 7/8/87 7/8/87 7/8/87 7/8/87 7/8/8/87 7/9/8/87 7/9/8/87 7/9/87 7/9/87 7/9/87 7/9/87	900 900 900 900 900 900 900 900 900 900	199.200000000000000000000000000000000000	1.37 1.37 1.57 1.55 1.55 1.55 1.55 1.53 1.53 1.53 1.53	1.6.6.6.0000000000000000000000000000000	0.05 0.05
78C2R 78D1F 78D2F 78D1R	7/8/87 7/8/87 7/8/87 7/8/87	1019 910 910 910	7/9/87 7/9/87 7/9/87 7/9/87	914 837 837 837	22.9 23.5 23.5 23.5 23.5	1.66 1.42 1.42 1.42	2.3 2.0 2.0	0.05
78D2R 78E1F 78E2F 78E3F 78E4F 78E1R 78E2R	7/8/87 7/8/87 7/8/87 7/8/87 7/8/87 7/8/87 7/8/87	910 737 737 737 737 737 737	7/9/87 7/9/87 7/9/87 7/9/87 7/9/87 7/9/87	837 713 713 713 713 713 713	23.6	1.42 1.71 1.74 1.76 1.76 1.71	2.0 2.5 2.5 2.2 2.3 2.7	0.05 0.05 0.05 0.04
78E3R 78E3R 78E4R 78F1F 78F2F 78F1R 79A1F 79A2F 79A2R 79A2R 79B1F 79B2F	7/8/87 7/8/87 7/8/87 7/8/87 7/8/87 7/8/87 7/9/87 7/9/87 7/9/87 7/9/87	737 737 824 824 824 1037 1037 1037 1037 953 953	7/9/87 7/9/87 7/9/87 7/9/87 7/9/87 7/9/87 7/10/87 7/10/87 7/10/87 7/10/87 7/10/87	713 713 800 800 800 931 931 931 931 953	3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.3.	1.76 1.76 2.35 2.25 2.35 2.25 1.57 1.47 1.47 1.47		0.39 0.32

Table 5 (cont.)

AZINPHOS-METHYL AMBIENT SITES RESULTS

SAMPLE ID	DATE START	TIME START	DATE STOP	TIME STOP	PERIOD (HOURS)	FLOW RATE (1pm)	AIR ( VOLUME ((Cu m)	AZINPHOS METHYL (Mg)
79B1R	7/9/87	953	7/10/87	853	23.0	1.66	2.3	
7932R	7/9/87	953	7/10/87	853	23.0	1.71	2.4	
79C2F	7/9/87	920	7/10/87	612	20.9	1.52	1.9	
79C1R	7/9/87	920	7/10/87	612	20.9	1.91	2.4	
79C2R	7/9/87	920	7/10/87	612	20.9	1.52	1.9	2 4 2
79D1F 79D2F	7/9/8 <b>7</b> 7/9/87	847 847	7/10/87 7/10/87	811 811	23.4 23.4	1.57 1.42	2.2 2.0	0.12
79D1R	7/9/87	847	7/10/87	811	23.4 23.4	1.42	2.2	0.1
79D2R	7/9/87	847	7/10/87	811	23.4	1.42	2.0	
79E1F	7/9/87	737	7/10/87	543	23.1	1.76	2.4	0.05
79E2F	7/9/87	737	7/10/87	643	23.1	1.76	2.4	0.05
79E3F	7/9/87	737	7/10/87	643	23.1	1.76	2.4	0.05
79E4F	7/9/87	737	7/10/87	643	23.1	1.76	2.4	0.05
79E1R	7/9/87	737	7/10/87	643	23.1	1.76	2.4	
79E2R	7/9/87	737	7/10/87	643	23.1	1.76	2.4	
79E3R	7/9/87	737	7/10/87	643	23.1	1.76	2.4	
79E4R 79F1F	7/9/87	737	7/10/87	643 70=	23.1	1.76	2.4	0.00
79F1F 79F2F	7/9/87 7/9/87	813 813	7/10/87 7/10/87	725 725	23.2 23.2	2.35 2.35	3.3 3.3	0.08 0.07
79F1R	7/9/87	813	7/10/87	725	23.2	2.35	3.3	0.07
79F2R	7/9/87	813	7/10/87	725	23.2	2.35	3.3	
713A1F	7/13/87	1435	7/14/87	1028	19.9	1.57	1.9	
713A2F	7/13/87	1435	7/14/87	1028	19.9	1.57	1.9	
713A1R	7/13/87	1435	7/14/87	1028	19.9	1.57	1.9	
713A2R	7/13/87	1435	7/14/87	1028	19.9	1.57	1.7	
713B1F	7/13/87	1245	7/14/87	930	20.8	1.18	1.5	
713B2F 713B1R	7/13/87	1245	7/14/87	930	20.8	1.47	1.8	
71381R 71382R	7/13/87 7/13/87	1245 1245	7/14/87 7/14/8 <b>7</b>	930 930	20.8 20.8	1.18 1.47	1.5	
71362F	7/13/87	1218	7/14/87	621	18.1	1.57	1.7	
713C1R	7/13/87	1218	7/14/87	621	18.1	1.62	1.7	
713C2R	7/13/87	1218	7/14/87	621	18.1	1.57	1.7	
713D1F	7/13/87	1118	7/14/87	833	21.3	1.37	1.7	
713D2F	7/13/87	1118-	7/14/87	833	21.3	1.37	1.7	0.06
713D1R	7/13/87	1118	7/14/87	833	21.3	1.37	1.7	
713D2R	7/13/87	1118	7/14/87	833	21.3	1.37	1.7	
713E1F	7/13/87	1100	7/14/87	700	20.0	1.71	2.1	
713E2F 713E3F	7/13/8 <b>7</b> 7/13/87	1100 1100	7/14/8 <b>7</b> 7/14/87	700 700	20.0 20.0	1.62 1.81	1.9 2.2	
713E3F	7/13/87	1100	7/14/87	700	20.0	2.00	2.4	
713E1R	7/13/87	1100	7/14/87	700	20.0	1.71	2.1	
713E2R	7/13/87	1100	7/14/87	700	20.0	1.62	1.9	
713E3R	7/13/87	1100	7/14/87	700	20.0	1.81	2.2	
713E4R	7/13/87	1100	7/14/87	700	20.0	2.00	2.4	
713F1F	7/13/87	1145	7/14/87	750	20.1	1.95	2.4	
713F2F 713F1R	7/13/87	1145	7/14/87	750 750	20.1	2.15	2.6	
713FIR 713FER	7/13/87 7/13/87	1145 1145	7/14/87 7/14/87	750 750	20.1 20.1	1.96 2.15	2.4 2.5	
714A1F	7/14/87	1143	7/15/67	1457	27.9	1.57	2.5	
				18	· · ·	→ • ••··		

Table 5 (cont.)
AZINPHOS-METHYL AMBIENT SITES RESULTS

SAMPLE ID	DATE START	TIME START	DATE STOP	TIME STOP	PERIOD (HOURS)	FLOW RATE (lpm)	VOLUME	AZINPHOS METHYL (µg)
			7/15/87 7/15/87 7/15/87 7/15/87 7/15/87 7/15/87 7/15/87 7/15/87 7/15/87					0.05
				19				

Table 5 (cont.)
AZINPHOS-METHYL AMBIENT SITES RESULTS

SAMPLE ID	DATE START	TIME START	DATE STOP	TIME STOP	PERIOD (HOURS)	FLOW RATE (lpm)	VOLUME	AZINPHOS METHYL (µg)
715F1F 715F2F 715F1R 715F2R 716A1F	7/15/87 7/15/87 7/15/87 7/15/87 7/16/87	1133 1133 1133 1133 1135	7/16/87 7/16/87 7/16/87 7/16/87 7/17/87	900 900 900 900 900 828	21.5 21.5 21.5 21.5 21.5	1.96 1.96 1.96 1.96 1.66	2.5 2.5 2.5 2.5 1.9	
716A2F 716A1R 716A2R 716B1F 716B2F	7/16/87 7/16/87 7/16/87 7/16/87 7/16/87	1315 1315 1315 1157 1157	7/17/87 7/17/87 7/17/87 7/17/87 7/17/87	828 828 828 743 743	19.2 19.2 19.8 19.8	1.66 1.66 1.66 1.57	1.9 1.9 1.9 1.9	
716B1R 716B2R 716C2F 716C1R	7/16/87 7/16/87 7/16/87 7/16/87	1157 1157 1120 1120	7/17/87 7/17/87 7/17/87 7/17/87	743 743 550 550	19.8 19.8 18.5 18.5	1.57 1.52 1.47 1.57	1.9 1.8 1.6 1.7	
716C2R 716D1F 716D2F 716D1R 716D2R	7/16/87 7/16/87 7/16/87 7/16/87 7/16/87	1120 954 954 954 954	7/17/87 7/17/87 7/17/87 7/17/87 7/17/87	550 925 925 925 925	18.5 23.5 23.5 23.5 23.5	1.47 1.37 1.28 1.37 1.28	1.6 1.9 1.8 1.9	0.07 0.07
716E1F 716E2F 716E3F 716E4F 716E1R	7/16/87 7/16/87 7/16/87 7/16/87 7/16/87	806 806 806 806	7/17/87 7/17/87 7/17/87 7/17/87 7/17/87	655 655 655 655 655	22.8 22.8 22.8 22.8 22.8	1.62 1.62 1.66 1.57 1.62	2.2 2.3 2.1 2.2	
716E2R 716E3R 716E4R 716F1F	7/16/87 7/16/87 7/16/87 7/16/87	806 806 806 912	7/17/87 7/17/87 7/17/87 7/17/87	655 655 655 620	22.8 22.8 22.8 21.1	1.62 1.66 1.57 2.00	2.2 2.3 2.1 2.5	0.15
716F2F 716F1R 716F2R	7/16/87 7/16/87 7/16/87	912 912 912	7/17/87 7/17/87 7/17/87	620 620 620	21.1 21.1 21.1	2.08 2.00 2.08	2.6 2.5 2.6	0.16

Table 6. Comparison of Replicates for Ambient Sites -- Azinphos-methyl (ppt)

Stationary Sites												
Date	Bakersfield		sfield Shafter Wasco			Brown Scho	McFaring Rd.	land Learning Center		Pond Unified School		
	1	2	1	2	1	2	1	2	1	2	1	2
6/22								/2.9				
6/23										3.1		
6/24							6.0	5.2				
5/25					1.6	2.8	/6.1 2.9	/6.3 2.4	A	Α	1.9	1.8
5/29	2.6	1.8			1.6		/2.8 2.3	/2.6 2.3	3.2	2.8	1.2	
5/30							/2.7	/2.2 2.2				
7/1								1.5				
7/6												
7/7				2.2							1.3	1.3
/8							1.6	1.6	1.9	1.9	9.0	7.8
/9							/1.6 1.6	/1.9 1.6	4.3	3.9	1.9	1.6
/13							/1.6	/1.6		2.6		
/14							/1.6	/1.7				
/15							•	•				
/16									2.8	3.0	4.6	4.7

# A. Equipment malfunction

<sup>\*</sup>Four sampling replicates at this site.

Table 7. Azinphos-methyl Average Values for Replicates

		<u>P.P.T.</u>									
Date	Bakersfield	Shafter	Wasco		Farland Id. Learning Center	Pond Unified School					
6/22 6/23				2.9 <sup>A</sup>	3.1 <sup>à</sup>						
6/24 6/25 6/29 6/30	2.2		2.2 1.6 <sup>A</sup>	5.9 2.7 2.4 2.2	3.0	1.9 1.2 <sup>A</sup>					
7/1 7/6 7/7 7/8		2.2 <sup>A</sup>		1.5 <sup>A</sup>	1.9	1.3 8.4					
7/9 7/13 7/14				1.6	4.1 2.6 <sup>A</sup>	1.8					
7/15 7/16					2.9	4.7					

AOne replicate only

Date	Bakersfield	Chafees	117	Mc	Farland	Pond
	Bakersrield	Shafter	Wasco	Browning Rd. Learning School Center		Unified School
5/22				38 <sup>A</sup>		
/23					40 <sup>A</sup>	
/24				76		
/25			28	3 <i>5</i>		24
/29	28		21 <sup>A</sup>	31	39	16 A
/30				28_		
<b>'</b> 1	•			19 <sup>A</sup>		
5 -			•			
7		28 <sup>A</sup>				17
/8				22	25	109
9				21	53	23
/13					34 <sup>A</sup>	
14				21		
15						
16					38	60

AOne replicate only

# Sampling Precision

Table 8 contains the calculated data precision of the collocated samplers at the ambient sites. The precision was calculated from the following equation:

$$P = [Y - (Y + X)/2]/X \times 100$$

where P is the calculated data precision; Y is the concentration from duplicate sampler of collocated pair; X is the concentration from primary sampler of collocated pair. Precision for the ambient data set ranged from -15 to 38 percent. Four samplers were located at the McFarland Browning Road School monitoring site for the purpose of evaluating precision. The poorest precision of any pair of samples from this site was 11 percent. Another measure of sample variability is the replicate analysis data of spiked samples, included in the ARB analysis report in Attachment IV.

Data completeness for the entire data set was greater than 95% for the ambient samples, based on the number of valid samples analyzed divided by the total number of samples taken.

Table 8. Precision for Ambient Site Samples (percent) for Replicated Sampling

	P.P.T.									
Date	Bakersfield	Shafter	Wasco	McFarian Browning Rd. School	Learning Center	Pond Unified School				
6/22										
6/23										
6/24				1						
6/25			38	-2		-3				
6/29	-15			9	-6					
6/30										
7/1				•	,					
7/6										
7/7						0				
7/8 ,				0	0	-7				
7/9				, 0	-5	-8				
7/13										
7/14			•	3						
7/15										
7/16					4	1				

# Literature Cited

- (1) Pesticide Use Report. California Department of Food and Agriculture, Sacramento, California. 1985 Annual Report.
- (2) American Conference of Governmental Industrial Hygienists. "Documentation of the Threshold Limit Values and Biological Exposure Indices," 5th ed., 1986.

## Acknowledgments

We wish to acknowledge the technical assistance of Lynn Baker, Tom Parker and Mike Poore with the California Air Resources Board. This study was supported by contract funds from the California Air Resources Board. Mention of proprietary products is made for identification purposes only and does not imply endorsement by ARB.

Attachment IV

Analysis Method

Date: July 1, 1987

Revision No.: Prelim. Draft 1
Approved:

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#### Method NLS015

Standard Operating Procedure for the Determination of Azinphos Methyl in Ambient Air

#### 1. SCOPE

This document describes a method for the analysis of azinphos methy!

(Guthion, 0,0-Dimethyl-S-[4-0X0-1,2,3-benzo-triazin(4H)-y1 methyl]

phosphorodithicate) at concentrations normally found in ambient air.

The method was developed based on EPA and California Department of Food and Agriculture methods.

#### 2. SUMMARY OF METHOD

After sampling, the exposed teflon fliter and XAD-2 sorbant tube are desorbed with 2.0 milliliters of 80/20 isooctane/acetone mixture. Two microliters of the extract are injected using splitless mode technique into a gas chromatographic system equipped with a 12 meter DB-1 fused silica capillary column, N-P thermionic detector (TSD), and data system. The resultant peak is identified by a characteristic retention time and quantitated in reference to external standards. The identity of the component can be confirmed by use of a column of different characteristics, a detector of different selectivity, or, if sufficient material is present, by GC/MS.

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#### 3. INTERFERENCES/LIMITATIONS

- 3.1 Since sampling is outside the scope of this document, sampling techniques, equipment, and conditions will not be discussed.
  Sampling capture efficiency studies have not been performed for the preparation of this SOP.
- 3.2 Compounds responding to the TSD detector and having similar GC retention times may interfere, causing misidentification and/or erroneous quantitation.
- 3.3 To insure minimum losses during storage, all samples received by the laboratory must be placed in a freezer operating at -4 degrees Centigrade or lower.

#### 4. APPARATUS

- 4.1 Varian Mode! 3300 Gas Chromatograph equipped with a thermionic detector (TSD) and Spectra Physics Mode! 4270 integrator.
- 4.2 DB-1 fused silica capillary column, 12 meters x 0.25 mm l.d.,
  0.5 um film thickness.

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4.3 Glass desorption vials, 3.7 ml capacity, with tefion-lined septum caps.

- 4.4 Sample agitator with timer and sample rack.
- 4.5 Microliter syringes, 5-50 ul sizes.

#### 5. REAGENTS

- 5.1 80/20 Isooctane/acetone desorbant solvent: Mix 800 ml pesticide grade isooctane (trimethyl pentane) and 200 ml pesticide grade acetone in a clean amber glass bottle equipped with a teflon-lined screw cap. Add to this mixture 1 ml of 2.0 mg/ml benzoxylldine surrogate mixture. CAUTION: FLAMMABLE.
- 5.2 Surrogate Mixture: Dissolve 100 mg of ACS Grade benzoxylidine in pesticide grade acetone and dilute to 50.0 ml.
- 5.3 Stock Standard: Commercially available certified solution of 1000 ug/ml of azinphos methyl in methanol (Nanogens, Inc.).
- 5.4 Calibration Standard: Dilute 50 ul of the stock standard into 50.0 ml of desorbant solvent. This corresponds to 1.0 ug/ml.

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5.5 Control Sample: Dilute 10 ul of stock standard into 50.0 mi of desorbant solvent. This corresponds to 0.2 ug/ml.

#### 6. INSTRUMENT CONDITIONS

Column: 12 m x 0.25 mm i.d. DB-1 fused silica capillary column

Temperatures: Injector: 250 degrees Centigrade

Detector: 300 degrees Centigrade

Oven: 50 degrees Centigrade, initial; hold for

1 minute; ramp at 50 degrees Centigrade to

150 degrees Centigrade; ramp at 10 degrees

Centigrade/minute to 250 degrees Centigrade,

hold for 4 minutes

Flow Rates: Carrier: Hellum, 30 cc/minute at splitter, 0.8 minutes splitless hold, carrier velocity; 25 cm/second

Detector: TSD - Range 11, Attenuation x 1

Hydrogen: 4.5 cc/mlnute

Air: 200 cc/minute

Date: July 1, 1987

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## 7. INSTRUMENT CALIBRATION PROCEDURE

- 7.1 Before a standard solution can be analyzed, a system blank must be analyzed. Inject 2.0 ul of solvent. If the analysis indicates interferences or contamination, the solvent must be replaced and the problem solved.
- 7.2 A method blank must be analyzed every 12 samples. Select an unused filter and sorbant tube, desorb the blank samples and carry through the analysis procedure. If inteferences or contamination is noted, the source must be found and eliminated before the analysis of samples can continue.
- 7.3 Instrument calibration is performed by injection of 2.0 ul of the 1.0 ug/ml standard. The resultant chromatogram is used to calibrate the retention time and response factor of the azinphos methyl under the conditions of this procedure. Calibration standards must be run every 12 samples.

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7.4 Proper instrument calibration is checked by the analysis of a control sample. The control sample must be analyzed after each calibration and prior to the analysis of samples. The concentration resulting from this analysis must fall within the upper and lower warning limits (±2d) of the control sample known value. If a result falls outside these limits, the problem must be found and solved prior to the analysis of samples. Plot all control sample results on the method control chart.

7.5 Two unused sampling media are "spiked" with 1.0 ug of azinphos methyl for each group of samples received by the laboratory.

These method spikes must be carried through the analytical procedure with the field samples. Method recovery must be at least 80%.

#### 8.0 ANALYSIS OF SAMPLES

8.1 Remove the teflon filter from the filter holder with stainless steel forceps. Carefully roll the filter and place it into a 3.7 ml vial. The filter must be forced into the bottom of the vial with a clean glass rod to insure complete contact with the solvent.

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8.2 After removal of the end-caps from the sorbant tube, score the tube above the location of the retainer spring. Using the tool provided, break the tube and remove the retainer spring. Place the glass wool plug and the primary (400 mg) section of the sorbant into a 3.7 glass vial. Retain the secondary section for later analysis in the event that the analyte is detected in the primary section.

- 8.3 Place 2.0 ml of desorbing solvent into all vials, cap tightly and agitate for 45 minutes.
- 8.4 After desorption, inject 2.0 ul of each extract into the chromatographic system for analysis. Record all pertinent information in the instrument analysis log book and on the resultant chromatogram.
- 8.5 The results are recorded in micrograms per sample and are calculated as follows:

 $mlcrograms = ug/ml (found) \times 2 ml$ 

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# 9.0 METHOD SENSITIVITY, PRECISION AND ACCURACY

The method sensitivity, precision and accuracy are presented in Table 1. The data were generated using standards. Note that the MDL is presented in ug/ml and in ug/sample assuming a desorption volume of 2.0 ml. A sample chromatogram is shown in Figure 1.

#### 10.0 DESCRPTION EFFICIENCIES AND SAMPLE STABILITY

The primary section of XAD-2 sorbant tubes were spiked with 2.0 and 1.0 micrograms of azinphos methyl. Five each of the tubes were analyzed immediately to determine desorption efficiencies. Five each of the tubes were stored for ten days at -4 degrees Centigrade and analyzed. The results are shown in Table 2.

#### TABLE 1

# METHOD PRECISION, ACCURACY, AND SENSITIVITY

Azinphos Methyl, ug/ml 1.0 0.5 0.2 0.1 Relative Standard Deviation, % 9.6 8.8 11.0 4.8

Correlation Coefficient: 0.998 Slope: 0.976

Intercept: 0.021 ug/ml

Method Detection Limit: 0.025 ug/ml (0.05 ug/sample)

#### TABLE 2

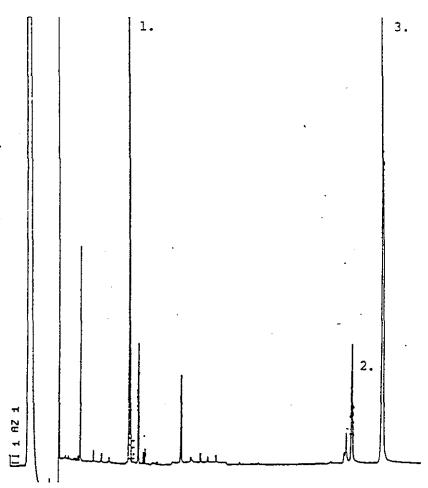
# SAMPLE STABILITY AND DESORPTION STUDIES

Desorption Efficiencies: 2.0 micrograms/sample:  $88 \pm 9 \%$  n=5 1.0 micrograms/sample:  $86 \pm 10 \%$  n=5

Recovery After Storage At -4°C (10 days):

2.0 ug/sample: 92  $\pm$  10 % n=5 1.0 ug/sample: 87  $\pm$  9 % n=5

FIGURE 1
AZINPHOS METHYL STANDARD CHROMATOGRAM



2.0 ul injection of 1.0 ug/ml azinphos methyl standard; splitless mode; 12m X 0.25mm i.d. DB-1 capillary column, 50°C, 1 min., 50°C/min to 150°C, 10°C/min to 250°C, 25cm/sec He, TSD @ 3.2 amps.

Compounds: (1) Surrogate, (2) Azinphos methyl oxon, (3) azinphos methyl

Attachment V
Quality Assurance Reports

# Memorandum

Bob Barham, Manager Toxics Program Support Section

Bob Effa, Manager

Quality Assurance Section

Monitoring & Laboratory Division

RECEIVED

Date :

Sept. 28, 1987

2:1987 TOO

Subject :

Evaluation of Azinphosmethyl

Monitoring

Stationary Sparce Division |

Air Resources Board

From : Air Resources Board

As you requested, we have conducted an audit of the azinphosmethyl air monitoring project. Our report is attached. The University of California Davis, responsible for the field sampling portion, was audited on July 7, 1987 in Kern County. The Monitoring and Laboratory Division, Northern Laboratory Branch, responsible for the analytical portion, was audited on July 14, 1987.

If you have questions regarding the azinphosmethyl air monitoring project, please call me at 322-3726, or Trene Del Real of my staff at 445-2555.

Peggy Vanicek Irene Del Real Bob Kuhlman Mike Poore

Attachment

#### Audit Report

# Azinphosmethyl Air Monitoring Project Bakersfield, California

September 28, 1987

# SUMMARY

## Field Audit:

On Tuesday, July 7, 1987 the Quality Assurance Section (QA) of the California Air Resources Board (CARB) performed a field audit of the azinphosmethyl air monitoring project which was being conducted in Kern County. The University of California at Davis (UCD) was responsible for the field sampling portion of the azinphosmethyl air monitoring project. Performing the audit were Bob Effa, Peggy Vanicek and Irene Del Real. Present from UCD was Mike McChesney.

A total of six sites were operated for the azinphosmethyl air monitoring project and all but two were audited. The audited sites included the Bakersfield ARB Station, Richland School District Office, Browning Road School and the Pond Union School District Office. Two sites not audited were McFarland Learning Center and the Engine Company #31 fire station. The field audits consisted of verifying conformance with the siting criteria, reviewing the site activity documentation and measuring the flow of the sampling devices. All the samplers audited were in conformance with the siting criteria. Documentation of the site activities and the sampling conditions were current and adequate for the air monitoring project. A flow audit of each sampling apparatus was conducted with a certified NBS traceable mass flowmeter. The reported flows of all samplers audited were within 15% of the standard flow as measured by the audit device.

# Laboratory Audit:

On Tuesday, July 14, 1987 a laboratory audit was conducted at the Monitoring and Laboratory Division, Northern Laboratory Branch which was responsible for the analytical portion of the azinphosmethyl air monitoring project. Mike Poore represented the laboratory and performing the audit were Peggy Vanicek and Irene Del Real of the Quality Assurance Section. The laboratory audit consisted of a systems audit and an analytical performance audit.

The systems audit consisted of a review of the laboratory operations and the quality control measures for sample handling, analysis and data documentation. No major deficiencies were found. Five Teflon filters and two adsorbant tubes were spiked by QA staff and submitted to the laboratory to be analyzed for the analytical performance audit. The laboratory's reported results were all within 32% of the assigned values. Described below in more detail are the field and laboratory audits followed by a comments section where any deficiencies noted are discussed.

# FIELD AUDIT

## Field Operations:

The six azinphosmethyl air monitoring sites were, the Bakersfield Air Resources Board (ARB) Station; the Richland School District Office; Engine Company #31 fire station; the McFarland Learning Center; Browning Road School; and, Pond Union School District. All the sites except the McFarland Learning Center and the Engine Company #31 fire station were audited on July 7, 1987 in Kern County. There was not access to the McFarland Learning Center, because the door leading to the site was locked on the scheduled audit date and the Engine Company #31 fire station was not audited due to safety reasons.

All the sites were collocated except for Browning Road School, which had four samplers instead of two. Each of the sampling sites were checked for conformance with the siting criteria outlined in the Stationary Source Division's (SSD) "Quality Assurance Plan for Pesticide Monitoring" dated June, 1986, along with a review of site maintenance and sample documentation. All the samplers audited conformed with the siting criteria except at the Richland School District Office where sampler #1 was within three meters of an air conditioner. Maintenance at each site was adequate although records for equipment maintenance were not easily accessed. Field documentation was kept in a bound notebook and included current records of sample collection dates, clock time, measured flow and average flow.

Adsorbant tubes and filters were collected daily and placed in a plastic bag and petri dish, respectively, which were then placed in a styrofoam ice chest containing dry ice. All the samples were transported to Sacramento in a private vehicle at the end of the week. Field record sheets or sample sheets were sent with the samples. Sample chain-of-cusody forms were not available for review and were not sent with the samples. Three weekly field blanks were included per 120 samples delivered to the laboratory. Field spikes were not being submitted to the laboratory; however, Mike McChesney stated that it was planned to include field spikes at a later date. On the day of the audit, the spiking procedure or exact date for beginning field spikes was not known.

#### Flow Audits:

The sampling apparatus consisted of a filter cassette containing a 47mm Gelmon Teflon filter with a small section of surgical tubing connecting it to a SKC XAD-2 adsorbant tube. Two sampling media were used to allow the collection of azinphosmethyl in both the particulate and volatile phases. During sampling each sorbant tube was vertically mounted and wrapped in aluminum foil to protect the sample from sunlight exposure. Tygon tubing connected the adsorbent tube to the HiVol pump. Sample flows were measured by UCD by using a Dwyer 1-4 L rotameter before and after sampling. No in-line flow controllers were used. The Dwyer rotameter was calibrated by the Monitoring and Laboratory Division's Quality Assurance Standards Laboratory in August 1986. Calibration data was not available in the field.

Flow accuracy audits were conducted using a Matheson Mass Flowmeter Model 8143 according to the procedures listed in Attachment 1. The mass flowmeter is certified against ARB's primary Standard Brooks Flow Calibrator. Results of the flow audits are summarized in Table 1. All of the UCD measured flows were within 15% of the standard flow as measured by the audit device.

TABLE I

Flow Accuracy Audit Results

Azinphosmethyl Air Monitoring Project

Site	UCD Measured Flow L/Min	ARB Standard Flow (L/min.)	Percent * Difference
Bakersfield ARB Station #1	1.4	1.22	+14.8
Bakersfield ARB Station #2	1.6	1.70	- 5.9
Richland School District Office #1	1.6	1.67	- 4.2
Richland School District Office #2	7.5	1.36	+10.3
Browning Road School #1	1.5	1.66	- 9.6
Browning Road School #2	1.7	1.80	- 5.5
Browning Road School #3	1.7	1.71	-0.6
Browning Road School #4	1.6	1.68	- 4.8
Pond Union School District Office #1	2.1	2.18	- 3.7
Pond Prion School District Office #2	1.9	1.96	- 3.1

<sup>\*</sup> Percent Difference = Measured Flow - Standard Flow x 100 Standard Flow

#### LABORATORY AUDIT

# System Audit:

Described below is a brief description of the system audit results.

# Laboratory Instrumentation:

Instrumentation used for the azinphosmethyl analysis was a Varian 3400 gas chromatograph utilizing a thermionic detector. Other analytical instrumentation included were a Varian 8034 autosampler and a Spectrophysics 4270 computer interface.

# Quality Control Measures - Sample Handling:

The University of California Davis was responsible for the sampling of azinphosmethyl. The sampling apparatus used was a SKC XAD-2 adsorbant tube with a small section of surgical tubing connecting it to a filter cassette containing a 47 mm Gelman Teflon filter with a 10 micron pore size. After sampling, the adsorbant tubes and filters were placed in a plastic bag and petri dish, respectively, and labeled by field personnel. Samples were collected daily and placed in a styrofoam ice chest containing dry ice. Each Friday, samples were delivered to the Monitoring & Laboratory Division, Northern Laboratory Branch and placed in a Freezer at -4°C until analysis. Sample record sheets and sample chain-of-custody forms were not included with the samples with the exception of a chain of custody form received for the last set of samples delivered. A copy of this chain-of-custody form is attached.

# Quality Control Measures - Sample Analysis:

The analytical procedure for the analysis of azinphosmethyl is documented in the Standard Operating Procedure (SOP) No. NLSO15 entitled "Standard Operating Procedure for the Determination of Azinphosmethyl in Ambient Air" (1 July 87, Revision No. Preliminary Draft 1). Laboratory staff developed the method based on EPA and California Department of Food and Agriculture Methods. A review of the procedure verified that the laboratory was conducting its analysis according to the procedure specified in NLSO15. Briefly, the method calls for desorbing the exposed XAD-2 sorbant tube or Teflon filter in 2.0 milliters of 80/20 isooctane/acetone mixture. Two microliters of the extract are injected into the gas chromatographic system. Additional details for this analytical method are found in the specified SOP. Method validation steps included the determination of the detection limit, sample storage stability and method recoveries. A detection limit of .05 ug/2ml was found, using the propogation of errors approach. Desorption efficiencies for adsorbant tubes was greater than 85% for 10 samples tested and recovery after storage at -4°C (10 days) was greater than 85% for 10 samples tested.

Quality control activities performed on a regular basis to monitor and document the laboratory data quality included a daily calibration and a daily standard analysis check after every twelve samples. A laboratory blank sorbant tube and filter was also analyzed after every twelve samples, respectively. Samples were analyzed in replicate (repeat analysis), to document analytical precision, when the sample's concentration was at least four times the detection limit. No studies were conducted on the stability of the standards which were prepared weekly from a Nanogen supplied stock standard.

Field quality control samples included three weekly field blanks with each delivery of 120 samples and field duplicates with all samples. No field spikes had been received prior to the laboratory audit date. On the day of the audit, one set of field spiked adsorbant tubes and filters were received but had not been analyzed. The field spikes were not blind, each sample was labeled with the spike concentration.

# Quality Control Measures - Documentation:

The laboratory assigned a unique sample number to each sample received and recorded the sample number in a bound notebook. Chain-of-custody procedures were not used. Sample record sheets were not utilized; however, the laboratory staff kept records of field samples in pencil on looseleaf paper. Bound notebooks were used in the laboratory to record instrument calibration and sample analysis information. Entries were made in pen and pencil and the bound notebook pages were not numbered. The audit team arbitrarily selected sample 11545 and followed the data trail from sample log-in to data reporting. The data were tracked successfully.

The laboratory sample record sheets recorded sample identification number, date sample received, date of analysis, type of sample, analyst and the results of the analysis. The recepient of the analytical data was not indicated on the record sheet.

#### ANALYTICAL PERFORMANCE AUDIT:

Spiked adsorbant tubes and spiked Teflon filters were submitted for analysis to evaluate the laboratory's analytical performance on both sampling media used in the field. The spiked samples were prepared by QA staff using the procedure outlined in Attachment II. Two sorbant tubes and five filters were spiked with one of two concentrations of azinphosmethyl. The concentrations were not known by the lab personnel. Table 2 contains a summary of the performance audit results. The reported values were within ± 32% of the assigned values. The analytical performance audit results demonstrated a positive bias in analyzing the Teflon filters. The adsorbant tubes showed very little bias.

TABLE 2
Azinphosmethyl Audit Results

# Monitoring and Laboratory Division Northern Laboratory Branch

# Laboratory Services

Sample Identification	Type	Measured Concentration (ug)	Assigned Concentration (ug)	Percent *
F-A	Teflon filter	0.27	0.206	+31
F-B	Teflon filter	0.05	Blank	-
F-C	Teflon filter	0.19	0.152	+25
F-D	Teflon filter	0.20	0.152	+32
F-E	Teflon filter	0.22	0.206	+ 6.8
T-A	XAD-2 Adsorbant tube	0.20	0.206	- 2.9
T-B	XAD-2 Adsorbant tube	0.75	0.152	- 1.3

<sup>\*</sup> Percent Bias = <u>Measured Concentration</u> - <u>Assigned Concentration</u> x 100

Assigned Concentration

#### FIELD AUDIT COMMENTS

Based on the field audit results, QA staff identified six items which would improve the azinphosmethyl sampling operation. They are the following:

#### Equipment Maintenance

All equipment maintenance entries and any comments should be entered in the field notebook in such a manner that the maintenance records are easily accessed. This documentation is necessary to trace any data abnormalities that may have been caused by equipment failure or changes.

# 2. Field Blanks

Field blanks should be included with each daily collection of samples to document any sample contamination that may occur during sample handling and transport.

# 3. Field Spikes

Field spikes should be included when possible with each set of samples submitted to the laboratory to document sample recoveries. It is recommended that the concentrations of the field spikes be unknown to the laboratory operator to prevent any bias on the part of the operator.

# 4. Field Record Sheets

Field record sheets should accompany the samples to the laboratory and include as a minimum the sample identification, sample collection date and the volume sampled.

# 5. Chain of Custody Record

It is recommended that chain-of-custody records should accompany the delivery of samples to document the sample custody process from sample collection to sample delivery.

# 6. <u>Teflon Tubing</u>

It is recommended that Teflon tubing be used in place of the surgical tubing since Teflon tubing is less porous than surgical tubing.

# LABORATORY AUDIT COMMENTS

Based on the laboratory audit results, QA staff identified three items which would improve the azinphosmethyl laboratory analysis operation. They are the following:

# 1. Laboratory Notebooks

All results of analyses entries and any comments should be made in the laboratory notebook in ink and initialed by the operator after each entry. Additionally, all other records for samples should be in ink and in a bound notebook.

# 2. Standard Stability

Standard stability studies should be conducted during method validation to document the standards stability.

# Confirmation

Confirmation is recommended using GC/MS or using another GC having a different column/detector for 10% of the samples to confirm the identification of azinphosmethyl.

#### Flow Audit Procedure for Pesticide Samplers

Introduction The pesticide sampler is audited using a Matheson Mass Flow Meter, Model 8143, that is standardized against a NBS traceable Brooks flow calibrator corrected to 25°C and 760 mm Hg.

The mass flow meter (MFM) is placed in series with the sample probe and the flows checked while the sampler is operating at the normal sampling flow rate. The standard (true) flow rates are obtained from the calibration curve of the MFM and the indicated flow rates are applied to the sampler's calibration curve to determine the reported flow rates which are then compared to true flow rates.

<u>Equipment</u> The basic equipment required for the pesticide sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

- 1. Matheson Mass Flow Meter, Model 8143, transfer standard with a 3 SLPM transducer.
- 2. Filter adapter for connection to sampler.
- 3. Teflon tubing, 1/4" I.D.
- 4. Stainless steel Swaglok fittings, cleaned with methanol and heated overnight at 100°C.
- 5. Plastic caps to cover flow meter ports.
- Audit log book and data sheets.

# Audit Procedures

- 1. Plug the Matheson MFM into a 110 VAC outlet. Allow 10 minutes for the MFM to warm up.
- 2. Connect the MFM to the sample tube using the filter adapter and 1/4" teflon tubing.
- 3. Allow the flow to stabilize for 1-2 minutes and record the indicated flows on the data sheet.
- 4. Apply the indicated flows to the calibration curve of the Matheson MFM standard to obtain the true flow and record in the blanks provided on the field data sheet. Obtain the sampler measured flow from the field operator. Calculate the difference between the true flow and measured flow and report as percent difference on the field data sheet.

Procedure for the Preparation of Azinphosmethyl Spike XAD-2 Adsorbant Tubes and Teflon Filters for the Pesticide Laboratory Performance Audit

# Introduction

The following equipment will be necessary to prepare spiked filters and adsorbant tubes. In addition, it is expected that the person preparing the spiked samples will abide by safe laboratory practices and use proper caution when dealing with azinphosmethyl.

- 1. Standards: Azinphosmethyl standard is obtained from Chem Services, Inc..
- 2. Glassware: All glassware is washed with soap and water, rinsed with deionized water followed by a methanol rinse.
- 3. Solvents: 80/20 isooctane /acetone mixture. Solvents are to be provided by the laboratory performing the analysis to minimize matrix differences.
- 4. Filters: 47 mm Gelmon Teflon filters.
- 5. Adsorbant tubes: XAD-2 SKC adsorbant tubes.
- 6. Filter Holders.
- 7. Analytical Balance: Mettler AE160 microbalance.
- 8. Petri dishes capable of holding 47 mm filters.
- 9. Log book.

#### Safety Precautions

Azinphosmethyl is considered poisonous.

Observe the following precautions:

- 1. Avoid skin contact with azinphosmethyl whether in solvent or as a solid. The use of protective gloves is recommended. If azinphosmethyl comes in contact with the skin, wash thoroughly and immediately with soap and water. Call a physician for further advice. Do not attempt self-treatment.
- 2. Use chemicals only in an exhaust-hood and keep bottles closed except when in actual use.

#### Standard Preparation

 Stock Standard: Dissolve 0.2534 grams azinphosmethyl in 50 ml 80/20 isooctane/acetone.

<u>. 10.</u>

- 2. High Concentration Spike: 200 ul azinphosmethyl stock standard is diluted to 50ml (20.67 ug/ml).
- 3. Low Concentration Spike: 150 ul azinphosmethyl stock standard is diluted to 50 ml (15.50 ug/ml).

#### Sample Preparation

- 1. Install filter in filter cassette and label.
- 2. Using a gas tight microliter syringe, place 10 ul of the appropriate spike standard solution, slowly, onto the filter. Do not exceed 10 ul of spiking liquid on the filter.
- .3. Using a gas tight microliter syringe, place 10 ul of the appropriate spike standard solution slowly into the adsorbant tube without coming in contact with the adsorbant tube walls. Do not exceed 10 ul of spiking liquid on the filter.
- 4. Prepare a blank filter using 10 ul of the 80/20 isooctane/acetone mixture.
- 5. Prepare a blank adsorbant tube using 10 ul of the 80/20 isooctane/acetone mixture.
- 6. Allow the spiked filters and adsorbant tubes to dry at room temperature.